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PREPARATION OF HIGH VISCOSITY WATER-SOLUBLE POLYCATIONICS

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This invention relates to a process of preparing high-viscosity water-soluble polymers from solutions of vinyl pyridinium salts.

For many applications water-soluble polymers of high viscosity give much better results than the same water-soluble polymers of lower viscosities. This is especially true for uses as a flocculant, retention aid, etc. Prior art processes have been inadequate either from the standpoint of process of properties of the product, or both.

An object of the present invention is a process of preparing high-viscosity water-soluble polymers from solutions of vinyl pyridinium salts. A further object is such a process wherein said salts are polymerized in aqueous solutions. An additional object is such a process wherein said salts are those derived from 2-methyl-5-vinyl pyridine, e.g. 1,2-dimethyl-5-vinyl pyridinium methyl sulfate. The above and other objects will be apparent from the description of this invention given hereinafter.

The above and other objects are accomplished according to the present invention by carrying out the process which comprises dissolving a water-soluble monomeric vinyl pyridinium salt in a solvent therefor to a concentration of at least about 50% and allowing the monomer to polymerize at a temperature not above about 30° C. According to a preferred embodiment of this invention, the solvent for the monomer is water and the polymerization is carried out in the presence of a catalyst and in the substantial absence of air. More specifically preferred is a monomer concentration of 65%–85% and a potassium persulfate ($K_2S_2O_8$) catalyst concentration of 0.001–0.008. Excellent results have been obtained with 75% 1,2-dimethyl-5-vinyl pyridinium methyl sulfate and 0.004% potassium persulfate dissolved in water and polymerized at 25° C. with a nitrogen cover, all percentages being by weight based on the monomer.

The following examples illustrate specific embodiments of the present invention. In these examples and elsewhere herein, the percent monomer and all parts are by weight; all other percentages are likewise by weight and, in addition, are based on the amount of monomer used.

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The process used in carrying out these examples was as follows: The monomer and catalyst, when a catalyst was used, were dissolved in water. In most examples air was removed from the polymerization reaction vessel (polyethylene bottles and tubes) and this was done by replacing the air with nitrogen. The polymerization was carried out in the aqueous solution under the temperature and time conditions specified. The polymerization gives a polymer in the form of a rubber-like gel. Various process and product data are given in Table 1 below.

In the examples of Table 1, the conversions were determined by U.V. analysis on aqueous solutions of the polymer product. Reduced specific viscosities (RSV) were determined in Ubbelohde viscometers (No. 1) using 0.500% solutions of the polymer product in 0.200 M aqueous sodium chloride. In each of the examples in Table 1, the monomer used was 2-methyl-5-vinyl pyridine and this was converted to its pyridinium salt by reacting with dimethyl sulfate. Preparation of this salt from the monomer is well known in the art. In each of the examples in Table 1, 100 parts of the monomer were used.

TABLE 1

Preparation and Properties of High Viscosity Poly(1,2-Dimethyl-5-Vinyl Pyridinium Methyl Sulfate)

Example No.	Monomer conc., percent	Water, percent	$K_2S_2O_8$, percent	Cover	Bath temp., ° C.	Reaction time, days	Conversion, percent	RSV	Variable
1	86	16.7	0.0080	Air	25	1	95	16.5	Monomer conc.
2	75	33.3	0.0080	do	25	1	95	14.5	Do.
3	65	58.1	0.0080	do	25	3	95	12.3	Do.
4	55	81.8	0.0080	do	25	5	94	8.6	Do.
5	75	33.3	0.00040	Nitrogen	25	3.8	92	27.8	Catalyst conc.
6	75	33.3	0.0020	do	25	3.8	100	26.9	Do.
7	75	33.3	0.010	do	25	3.8	100	22.9	Do.
8	75	33.3	0.020	do	25	3.8	100	21.7	Do.
9	75	33.3	0.050	do	25	3.8	100	16.3	Do.
10	75	33.3	0.10	do	25	3.8	100	11.4	Do.
11	75	33.3	0.30	do	25	3.8	100	8.61	Do.
12	75	33.3	0.50	do	25	3.8	100	4.52	Do.
13	75	33.3	1.0	do	25	3.8	100	4.85	Do.
14	75	33.3	None	Air	25-30	3	98	17.2	Do.
15	75	33.3	0.0040	do	0	1	66	--------	Temperature.
16	75	33.3	0.0040	do	25	3	91	25.0	Removal of air.
17	75	33.3	0.0040	Nitrogen	25	3	91	--------	Do.
18	75	33.3	0.0040	Air	25	1.3	88	26.6	Do.

Although specific embodiments of the present invention are set forth in the foregoing examples, and other disclosures, this is not intended to limit the invention other than as defined in the claims hereof. The invention broadly comprises dissolving a water-soluble monomeric vinyl pyridinium salt in a solvent therefor to a concentration of at least about 50% and allowing the monomer to polymerize at a temperature of not above about 30° C.

The present invention is applicable to solution polymerization (including copolymerization) of monomeric water-soluble vinyl pyridinium salts including, but not limited to, those derived from 2-vinyl pyridine, 4-vinyl pyridine, 2-methyl-5-vinyl pyridine (e.g. 1,2-dimethyl-5-vinyl pyridinium methyl sulfate), 2-vinyl-5-ethyl pyridine.

Although water serves quite well as a solvent for the monomer, and one therefore normally would have no reason for desiring any other solvent, other solvents will work provided they are inert and will dissolve high concentrations of the monomer. For instance, mixtures of acetone or methanol with water work very satisfactorily.

The concentration of monomer must be high to give polymers of high viscosity. We have found that such concentration must be at least about 50% by weight and preferably 65%–85%. This will vary somewhat with the particular monomer as well as the other conditions employed. We have obtained excellent results using a concentration of 75% monomeric 1,2-dimethyl-5-vinyl pyridinium methyl sulfate in water, this concentration being